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**FUNDAMENTAL STUDIES OF NEURAL STIMULATING ELECTRODES**

**Twelfth Quarterly Report  
Covering Period May 29, 1997 to August 28, 1997**

**CONTRACT NO. N01-NS-4-2310**

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This QPR is being sent to  
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## TABLE OF CONTENTS

SECTION		PAGE
1.	INTRODUCTION AND SUMMARY .....	4
2.	VOLTAMMETRIC STUDIES ON IR MICROELECTRODES.....	5
3.	AC IMPEDANCE STUDIES OF AIROF CHARGE INJECTION ELECTRODES .....	7
4.	FUTURE WORK.....	11

## LIST OF FIGURES

FIGURE		PAGE
2-1	Diagrammatic representation of sites and site identification on U. Michigan ribbon-cable probe.....	5
2-2	Apparent capacitance of site 1 on U. Michigan ribbon-cable probe No. 1 at 200 V/s for the 30 scan rate studies.....	6
2-3	Voltammetric scans of site 1 on U. Michigan ribbon cable probe No.1 after 59, 160, 354, 517, 619 and 727 days of soaking.....	6
3-1	The effect of potential on the AC impedance of activated Ir.. .....	9
3-2	AC impedance of three AIROF electrodes. Electrode BAS is activated to 44 mC/cm <sup>2</sup> and 104 mC/cm <sup>2</sup> for comparison of the effect of CSC .....	10
3-3	AIROF cyclic voltammograms of electrodes shown in Fig 3-2.....	10

## 1. INTRODUCTION AND SUMMARY

This report describes work on NINDS Contract No. N01-NS-4-2310 during the period May 29, 1997 to August 28, 1997. As part of the Neural Prosthesis Program, the broad objectives of the present fundamental studies are: 1) to evaluate the electrochemical processes that occur at the electrode-electrolyte interface during pulsing regimens characteristic of neural prosthetic applications; 2) to establish charge injection limits of stimulation electrode materials which avoid irreversible electrochemical reactions; 3) to develop an *in vitro* method, which can be applied *in vivo*, for determining the electrochemical real area and stability of microelectrodes; 4) to develop new materials which can operate at high stimulation charge densities for microstimulation; and 5) to provide electrochemical and analytical support for other research activities in the Neural Prosthesis Program at NINDS.

The contract has been granted a no-cost-extension to December 31, 1997. During this period, work will focus on the completion of AC impedance studies and the preparation of a manuscript on activation of Ir to AIROF.

During the current reporting period, long term studies of U. Michigan ribbon-cable-probe No. 1, site 1 were continued. The apparent capacitance of the inactivated site, calculated from the current at 0.0 V vs. Ag|AgCl in a 200 V/s potential sweep, has been monitored for over 727 days of soaking in PBS. An abrupt but modest increase in the capacitance from 0.5 nF to ~2.5 nF was observed at day 91 of the soak test. On day 217, the electrode was inadvertently allowed to dry out. After the electrode was rehydrated, the apparent capacitance had decreased to a value closer to that observed before day 91. There has been no increase in  $C_{app}$ , similar to that observed at day 91, for the 510 days of soaking since the electrode was rehydrated at day 217.

## 2. VOLTAMMETRIC STUDIES ON Ir MICROELECTRODES

During this quarter we continued studies of the long term stability of Ir sites on a probe with an integrated ribbon cable received from U. Michigan. Figure 2.1 is a diagrammatic representation of the probe showing the numbering scheme for the electrode sites. The probe has been under soak in phosphate buffered saline (PBS) for 727 days.

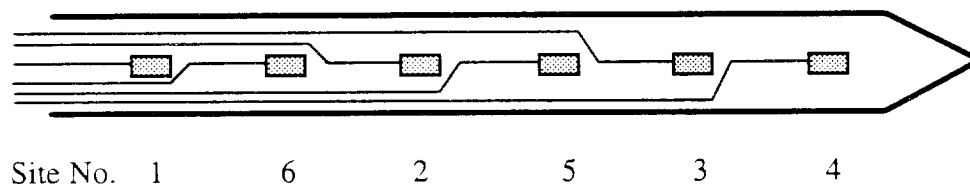


Figure 2.1 Diagrammatic representation of sites and site identification on U. Michigan ribbon-cable probe.

Measurements of the apparent capacitance of site 1 of the ribbon-cable-probe No. 1 were continued. Test procedures and results are detailed in previous Quarterly Progress Reports (Nos. 5-11). The apparent capacitance,  $C_{app}$ , at 200 V/s, is plotted in Fig. 2-2 as a function of time for the study performed this quarter along with data from the 30 studies conducted during the previous seven quarters.  $C_{app}$  is calculated by dividing the current at 0.0 V vs. Ag|AgCl by the scan rate, thus  $C_{app} = Q/V = i/v$ , where  $v$  is the scan rate.

We do not have a satisfactory explanation for the increase in apparent capacitance between days 91 and 220. The inadvertent drying out of the electrode at day 217 presumably caused the decrease in  $C_{app}$ . However, there has been no increase in  $C_{app}$  similar to that observed at day 91 for the 510 days of soaking since the electrode was rehydrated at day 217. This result, and the abruptness of the increase observed at day 91, suggests that the increase in  $C_{app}$  is not due to an ongoing degradation process at the electrode site.

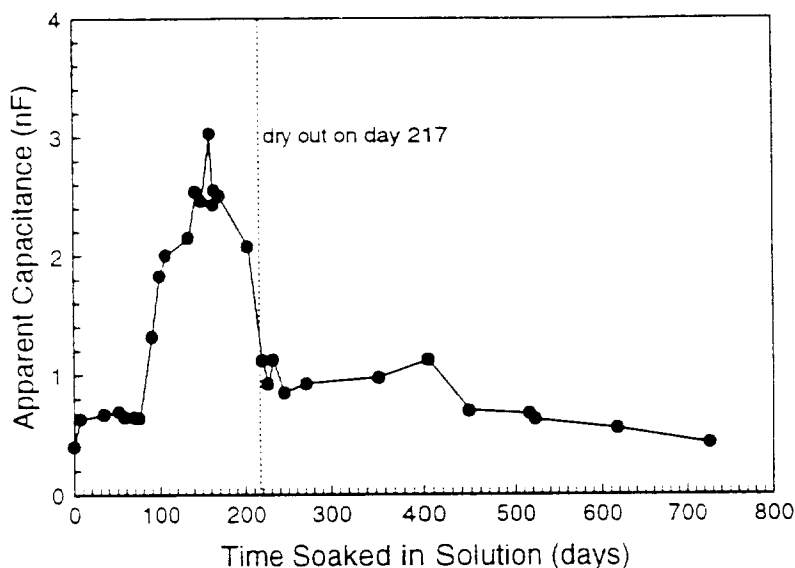


Figure 2-2 Apparent capacitance of site 1 on U. Michigan ribbon-cable probe No. 1 at 200 V/s for the 30 scan rate studies.

A comparison of the voltammetric scans used in the calculation of  $C_{app}$  at 200 V/s for days 59, 160, 354, 517, 619 and 727 is shown in Fig. 2-3. The 59, 354, 517, 619 and 727 day scans are not significantly different. This site has exhibited a stable electrochemical response for more than one year of soaking in 0.1M PBS.

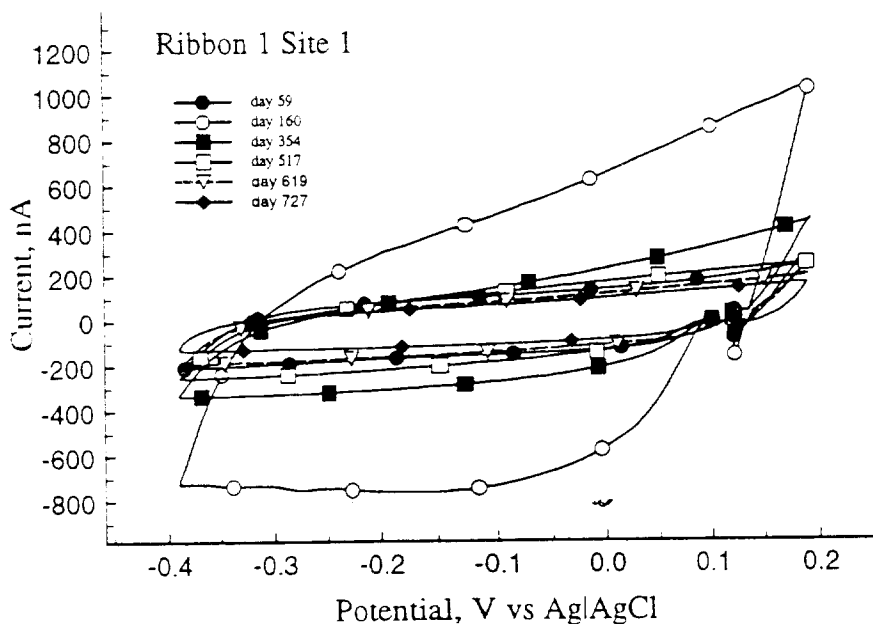


Figure 2-3 Voltammetric scans of site 1 on U. Michigan ribbon cable probe No.1 after 59, 160, 354, 517, 619 and 727 days of soaking. Scan rate = 200 V/s.

### 3. AC IMPEDANCE STUDIES OF AIROF CHARGE INJECTION ELECTRODES

There is a need to develop an *in vivo* testing procedure that periodically assures the performance of implanted FES electrodes, especially for those electrochemically activated iridium "oxide" electrodes where the integrity of the electrodes may be compromised or at best the quantity of "oxide" altered, consequently changing the safe charge injection limits. Impedance spectroscopy has the potential to provide such a testing procedure. Thus, the identification and characterization of the processes that go on during charge/discharge of activated iridium "oxide" films is important.

Glarum and Marshall have applied the small-signal ac technique to the case of iridium oxide coated electrodes in an unbuffered acidic medium<sup>1</sup>. An equivalent circuit was devised for the data and a mechanism of charge/discharge processes proposed. The experimental data do not fully comply with the suggested circuit, and a model for a "highly porous film with essentially all oxide sites accessible to an electrolyte phase" was invoked.

In the Ninth Quarterly Report, it was verified that iridium "oxide" formation is influenced by:

- the chemical composition of the electrolyte;
- the geometry and morphology of iridium metal substrate;
- the duration and form of the perturbation signal.

Specifically, the electrolyte composition influences the rate of formation and the oxide morphology through the pH, the ionic strength, the conductivity and the structure of the electrical double layer.

During a constant current or potential perturbation of an electrode/electrolyte system, a non-uniform current distribution occurs at the electrode that depends on the finite conductivity of the

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<sup>1</sup> S. H. Glarum and J. H. Marshall, "The A-C Response of Iridium Oxide Films," J. Electrochem. Soc., **127**, 1467, (1980).

electrolyte solution, the electrode geometry and porosity of the electrode material, the perturbation signal and the time. The current distribution, then, will impact on the rate of formation of the oxide, its morphology and ultimately the uniformity/non-uniformity of the electrode coverage.

An approach to select the procedure to optimize iridium "oxide" for a particular application seeks a mathematical description of the current-distribution for each system. Analytic solutions for the current distribution for the electrodes with the simple geometries are available but the description of electrodes used in neural prostheses, at best, must be obtained numerically. Nevertheless, some prevailing trends for the current-distribution can be qualitatively evoked from these existing solutions. Generally, the currents are lower at the less accessible part of the electrode, i.e., the current at the edges of the electrodes may vary between infinity and zero depending on the angle between the insulator and conductor. The current distribution can change with time during the electrochemical transient for the charging process, and after a "certain" time the current becomes uniform throughout the electrode. For a faradaic process, the current distribution (the gradient) is a more complex function of time and the accessibility factor<sup>2</sup> of the electrode is altered by the type of process encountered, that is, surface process, mass transport limited or electron transfer limited process. This gradient may never become zero during the transient, but decays with time. It is important to recognize from this that a more uniform surface coverage will be obtained with "longer" transients. The optimum pulse duration depends on the accessibility factor of the electrodes, particularly the quality of the insulator/metal seal.

In the Eighth Quarterly Report, it was demonstrated, based on steady-state ac impedance data, that non-porous oxide films of uniform thickness are formed on the surface of iridium electrodes in an aqueous electrolyte solution by continuously cycling the electrode potential with a triangular or square waveform of "low" frequency. In this quarter, impedance measurements were acquired

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<sup>2</sup>Notice, that accessibility factor depend not only on the shape of the electrode itself, but also on the geometry of the entire electrochemical cell, and particularly on the shape of the support on which the electrode is mounted.



for the iridium electrodes of different geometric dimensions and different levels of activation under various activation conditions.

The examples of impedance data acquired at different electrode potentials are illustrated in Fig. 3-1. The influence of activation conditions and electrode size on the impedance and cyclic voltammetric spectra are illustrated in Figs. 3-2 and 3-3, respectively. The detailed analyses of the data are in progress. The analysis of the data is lengthy and requires a cautious assessment of their applicability associated with the requirements of causality, linearity, stability and that the impedance must be finite and continuous between  $\omega(0)$  and  $\omega(\infty)$  associated with the system. If these provisos can be met, the outcome of the analysis should provide the essential data base for *in vivo* quality control of electrodes.

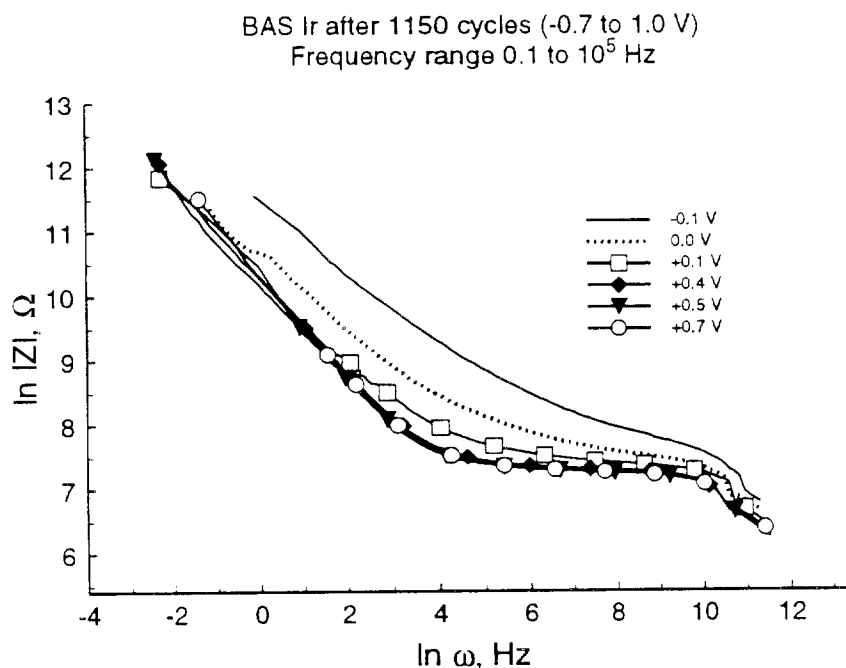


Figure 3-1. The effect of potential on the AC impedance of activated Ir.

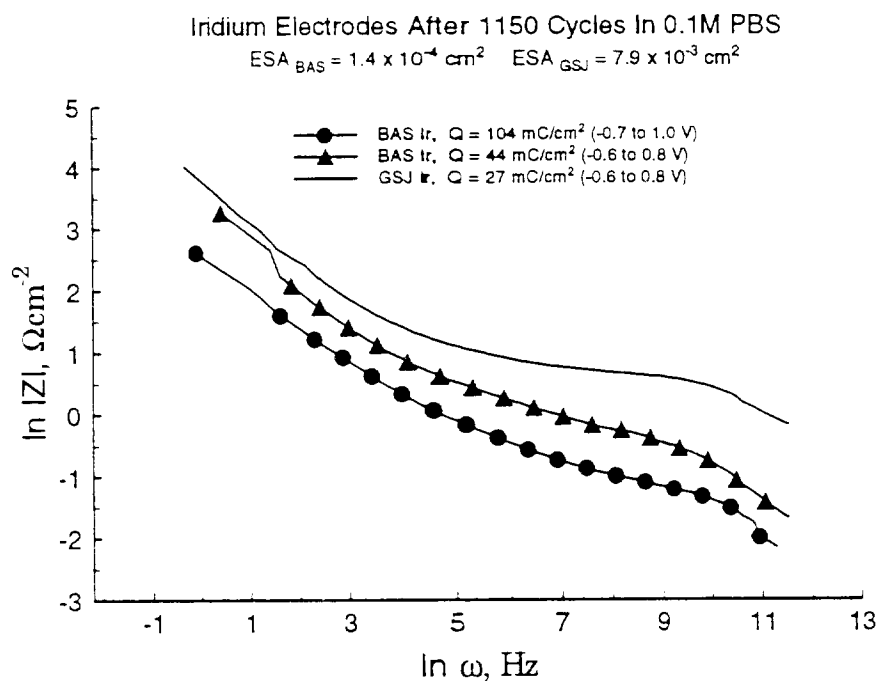


Figure 3-2. AC impedance of three AIROF electrodes. Electrode BAS is activated to 44  $\text{mC}/\text{cm}^2$  and 104  $\text{mC}/\text{cm}^2$  for comparison of the effect of CSC. Electrode GSJ has an electrochemical surface area of 50 times that of the BAS electrode.

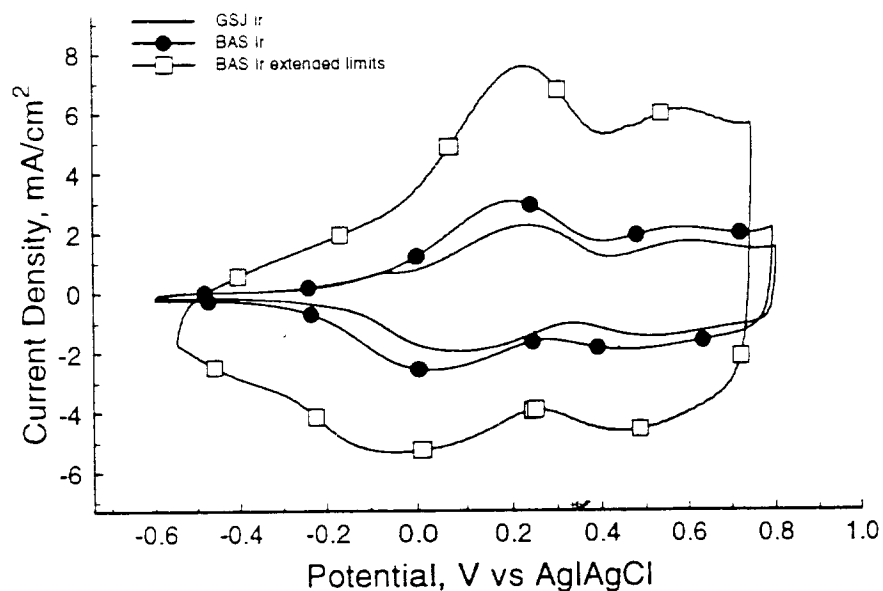


Figure 3-3. AIROF cyclic voltammograms of the electrodes shown in Fig 3-2. Sweep rate 50  $\text{mV}/\text{s}$ .

#### **4. FUTURE WORK**

The analysis of AIROF impedance data will continue in the next reporting period with emphasis on establishing the suitability of the technique for *in vivo* electrode evaluation.